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# Extensional viscosity and stability of oil-in-water emulsions with addition poly(ethylene oxide)

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**Abstract**

The main objective of this study was to investigate how polymer used as auxiliary emulsifier improves the stability of oil-in-water emulsions. Two kinds of polymeric emulsifier were used: poly(ethylene oxide) (PEO) and carboxymethylcellulose sodium salt (Na-CMC) with various average molecular mass weight. Therefore, the influence of PEO and Na-CMC on the creaming of oil-in-water emulsions has been investigated. Moreover, studies of extensional viscosity of emulsions and pure polymer solutions were made on the opposed-nozzle rheometer. In the case of emulsions stabilized with PEO the creaming of emulsion progressed slower in the case of polymer having an average molecular weight $M_w = 2 \cdot 10^6$, and faster for addition of PEO with the molecular mass $M_w = 8 \cdot 10^6$. However, for emulsions stabilized with Na-CMC the fastest creaming has been observed for polymer with a lowest molecular weight ($M_w = 2.5 \cdot 10^5$). The study reveals that there is no direct connection between the extensional viscosity of the continuous phase of emulsions and rate of creaming. This is mainly due to the fact that preparation of emulsion stabilized by addition of PEO with different average molecular weights and similar shear viscosity of the continuous phase was unfortunate.



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## 1. Introduction

Many food, pharmaceutical, cosmetic and chemical products exist in the form of emulsions, whereby one immiscible (dispersed) phase is distributed in another (continuous) phase. These can be oil-in-water (o/w), water-in-oil (w/o) or complex multiple emulsions (w/o/w or o/w/o). In general, they are thermodynamically unstable systems that tend to break down over time due to a variety of physicochemical mechanisms, for example, gravitational separation, creaming, flocculation and Ostwald ripening [1]. Therefore, a common issue of dealing with emulsions is their instability. Oil-in-water emulsions are stabilized by two main types of emulsifier agents, namely low molecular weight surfactants and water-soluble polymers [2,3]. Among water-soluble polymers, proteins [4,5] block copolymers [6,7], polysaccharides [8,9] and surface active homopolymers [10,11] are considered as suitable candidates for emulsifier agents to prepare oil-in-water emulsions, since they could form a thick adsorbed layer, which plays an important role in a protective layer. Furthermore, when polymers are present in the dispersion phase, its viscosity increases and the coalescence of droplets could be observed. Thus, some of the most significant aspects of the oil-in-water emulsions stabilized by polymer chains are polymer adsorption on oil-water interface and rheological properties of emulsion.

**Nomenclature**

| | |
|---|---|
| $R$ | radius of nozzle |
| $M$ | torque |
| $L$ | arm length |
| $h$ | distance between the nozzles |
| $\dot{V}$ | flow rate |
| $\dot{\varepsilon}$ | extension rate |
| $Tr$ | Trouton number ($Tr = \eta_E/\eta$) |
| $\eta_E$ | extensional viscosity |
| $\eta$ | shear viscosity |
| $\phi$ | volume fraction of oil |

Interaction between polymer and surfactant can change the adsorption layer around the oil droplets in emulsion, therefore, influencing emulsion stability. In authors' opinion, it seems that extensional viscosity might play significant role in the phenomenon of bringing emulsions' droplets to each other, therefore serving an important role in description of stability.

Solutions of high-molecular-weight polymers exhibit extension thickening in elongational flow. Particularly, it is observed for aqueous solutions of poly(ethylene oxide) (PEO) due to the flexible structure of the chain. The results of the extensional viscosity measurements performed for the solutions of PEO in the stagnation flow have been presented by Dontula et al. [12] and Gauri and Koelling [13].

Both groups of researches reported similar results, polyethylene oxide solutions were characterized by a very high value of the Trouton number (about 100 and higher).

Emulsion properties in shear flow with addition of poly(ethylene oxide) and sodium carboxymethyl cellulose (Na-CMC) were reported extensively by Pal [14,15]. Pal [14] studied the poly(ethylene oxide) with three different molecular weights ($M_w$ = $2{\cdot}10^5$; $6{\cdot}10^5$ and $4{\cdot}10^6$). Author [14] studied effects of polymer and oil concentrations on the viscous properties of emulsions. The polymer solutions and their emulsions were described by the Ellis model. The relative viscosities for polymer-thickened emulsions fall well below the corresponding relative viscosities for emulsions without polymer addition. The decrease in the relative viscosities for polymer-thickened emulsions was explained in terms of the viscosity ratio between the continuous phase viscosity ($\eta_c$) and the dispersed phase viscosity ($\eta_d$), namely $\eta_c/\eta_d$. The polymer-thickened emulsions have a high $\eta_c/\eta_d$ ratio and consequently, internal circulation within the dispersed droplets plays an important role in determining the relative viscosity.

Diftis and Kiosseoglou [16] investigated o/w emulsion stability with addition of soybean protein isolate (SBPI) and Na-CMC in ratio of 1/1 and 1/3. They showed that the stability against creaming of the emulsions prepared with soy protein alone is very poor. In the presence of non-treated (SBPI)- medium against with addition of Na-CMC mixtures, emulsion stability is higher for the last one. In that case the increased stability could be attributed to the viscosity of the continuous phase as a result of Na-CMC presence.

In this paper authors used two kinds of polymeric emulsifiers: poly(ethylene oxide) and carboxymethylcellulose sodium salt. Poly(ethylene oxide) resins are a very important class of the nonionic polymers especially known for their spectacular drag-reduction activity [16,17]. Moreover, PEO can be used as a matrix system for controlled release, a tablet binder for direct compression, a mucosal bioadhesive, a thickening agent, and a tablet coater [18]. These polymers behaved like an inert species in the emulsions, i.e. no flocculation or bridging of oil droplets was observed because the polymer imparted high viscosity and shear-thinning behavior to the emulsions.

The main goal of this work is to present the influence of PEO and Na-CMC additions on the o/w emulsion stability. Additionally, the investigation is supplemented with measurements and discussion of extensional and shear viscosities for aqueous solutions of polymer and emulsions.

## 2. Materials and methods

Mineral oils were obtained from Institute of Petroleum Technology (Kraków, Poland). The viscosity of the mineral oil was 0.2182 [Pa·s]. The measurements were carried out with o/w emulsions in concentration varying in the range from 20 to 40 vol.-% of dispersed phase (mineral oil).

Poly(ethylene oxide) and carboxymethylcellulose sodium salt were purchased from Sigma-Aldrich (Poland). Tween 40 was used as the emulsifier and its concentration in all prepared emulsions was equal to 5 vol.-%. Polyethylene oxide with three different average molecular weights ($M_w = 2{\cdot}10^6$; $5{\cdot}10^6$ and $8{\cdot}10^6$) and Na-CMC ($M_w$ = $7{\cdot}10^5$, $2.5{\cdot}10^5$) were used as polymeric emulsifiers. Used concentrations of polymer solutions are given in Table 1.

Table 1. Concentration of polymer used in the study

| Polymer | Molecular weight $M_w$ | Concentration $C_p$ (%) |
|---|---|---|
| Poly(ethylene oxide) | 2 000 000 | 0,5 |
| | 5 000 000 | 0,2 |
| | 8 000 000 | 0,13 |
| Carboxymethylcellulose sodium salt | 250 000 | 2,17 |
| | 700 000 | 0,4 |

Concentration of both Na-CMC and PEO solutions have been selected in such way that viscosity of their solutions at low shear rate were similar. Another reason for the selection of polymers for this research was the difference in emulsions structures observed with their addition. In the case of Na-CMC use the flocculi were formed while using PEO the distributed drops were found.

The rheological measurements in shear flow were carried out using a rotational rheometer Physica MCR 501 produced by Anton Parr (Germany) equipped with cone-plate measuring system. All measurements were performed at stabilized temperature of 20 °C.

## 3. Emulsion preparation

At first, specified amount of surfactant was dissolved in water and it was mixed mechanically for 2h in the tank equipped with four baffles and turbine impeller. Next, the required amount of oil was added and again it was mixed by 2h with the same equipment as before. Finally, aqueous solution of polymer, prepared previously by dissolving polymer in small volume of water, was added and everything was also mixed mechanically for 2 hours.

Due to the fact that the PEO chain has a specific structure and the ability to degrade under the influence of mechanical factors, the solutions were prepared by slow addition of an appropriate amount of compound to distilled water while stirring slowly. The solution was stirred for another 24 hours, using a slow-speed mixer to achieve a homogeneous mixture. In the same way all the solutions were prepared at various concentrations and molecular weights.

## 3. Set-up

The method of creating an approximated extensional flow field based on opposed jets was used. The detailed description of measuring set-up, the opposed nozzle rheometer, has been presented previously in [20]. The extension rate imposed on the fluid in rheometer is determined by the volumetric flow rate and by the geometry of the set-up:

$$\dot{\varepsilon} = \frac{\dot{V}}{\pi \cdot R^2 \cdot h} \tag{1}$$

Therefore, the extensional viscosity is then given by equation:

$$\eta_E = \frac{M}{\dot{\varepsilon} \cdot \pi \cdot R^2 \cdot L} \tag{2}$$

## 4. Determination of emulsion stability

Emulsion creaming was investigated in 1 liter glass cylinders at room temperature. The stability of the emulsion was conducted by visual monitoring of the separation of cream layer and serum layer over a period of 20 or 24 h. During the creaming test pictures were taken in one hour interval. Canon EOS 1D Mark III was used as camera, and it was connected to personal computer with installed Canon Utilities ZoomBrowser EX 5.8 software in order to record pictures.

Microstructure of the emulsions was studied at room temperature using Nikon Eclipse 50i polarized light microscope (Tokyo, Japan). The images of the droplets were captured through the CCD camera (OptaTech) mounted on an optical microscopy. A drop of emulsion was placed between a microscope

slide and cover slip. The captured images were analyzed using the Image ProPlus 6.1 image analysis software (MediaCybernetics, MD, USA).

## 5. Results and discussion

### *5.1. Shear and extensional flow*

Figures 1 and 2 show the viscosity curves of aqueous solutions of poly(ethylene oxide) and sodium carboxymethylcellulose. Polymer concentrations were adjusted in such way that at low shear rates the polymer solutions with different average molecular weights had similar viscosity values. From the data presented in Figure 1 it is evident that at shear rates above about 2 $s^{-1}$ the solution's viscosity of Na-CMC with the average molecular weight $M_w = 2.5 \cdot 10^5$ is higher than the viscosity of the solution with the average molecular weight $M_w = 7 \cdot 10^5$. Extensional viscosities of Na-CMC solutions in the extensional rate ranged between 1 and 100 $s^{-1}$ were comparable for both polymer solutions with different molecular weights. At higher values of shear rates there was an inverse trend in shear viscosity, whereas extensional viscosity of Na-CMC with $M_w = 7 \cdot 10^5$ was greater than of the polymer solution of $M_w = 2.5 \cdot 10^5$. The rheological properties were also obtained for 20% emulsions with addition of Na-CMC with two different average molecular weights which are presented in Fig. 2. Both, shear and extensional viscosities of emulsions are higher than the viscosity of the polymer solutions. The Trouton ratio has slightly smaller value for emulsion than for the pure polymer solutions (Fig. 2).

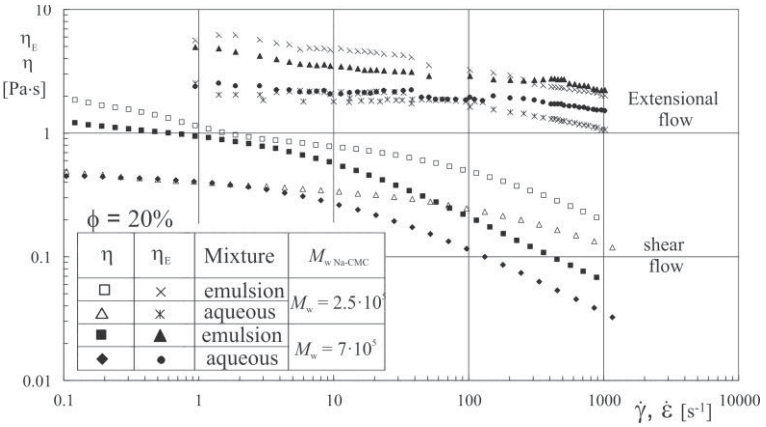


Fig. 1. Comparison of extensional and shear viscosities of aqueous polymer solutions and emulsion with addition of Na-CMC

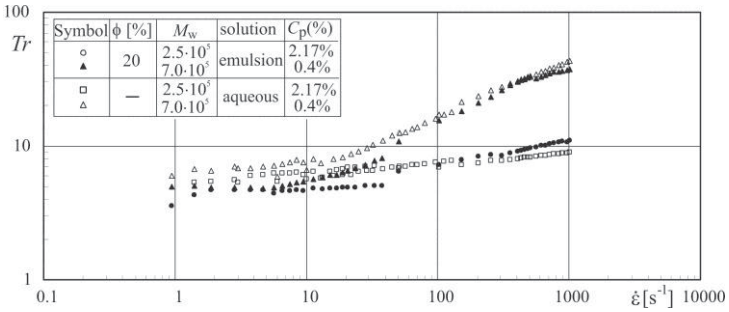


Fig. 2. Trouton ratio for emulsion with addition of Na-CMC and for pure solutions of Na-CMC

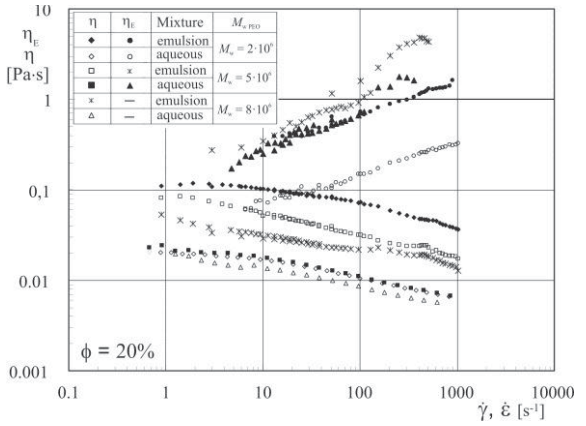


Fig. 3. Comparison of extensional and shear viscosity of aqueous polymer solutions and emulsion with addition of PEO

Contrasting results were obtained for emulsions stabilized by PEO. In this case, extensional viscosity increases with increase of extensional rate, whereas shear viscosity decreases with increase of shear rate. Additionally, extensional viscosity of PEO solution with average molecular weight of $5 \cdot 10^6$ was almost one magnitude bigger than for PEO with average molecular weight of $M_w = 2 \cdot 10^6$. The viscosity measurement of solution of PEO with $M_w = 8 \cdot 10^6$ was not done due to exceeding the measuring range of force in used rheometer. Figure 3 shows the flow curves for emulsions stabilized by the addition of PEO. The highest viscosity at shear was met in solution stabilized by polymer of an average molecular weight $M_w = 2 \cdot 10^6$, however, the lowest was found for $M_w = 8 \cdot 10^6$. The ratio of extensional viscosity of emulsion with PEO of $M_W = 2 \cdot 10^6$ to the extensional viscosity of the aqueous polymer solution was about 5. In the case of emulsions stabilized by polymer of $M_W = 5 \cdot 10^6$ that ratio drops to about 2.5.

### *5.2. Structure of emulsions*

Images of emulsion droplets structure stabilized by the addition of sodium carboxymethylcellulose with an average molecular weight of $M_w = 2.5 \cdot 10^5$ and PEO of molecular weight equal to $2 \cdot 10^6$ are presented in Fig. 4.

a) b)

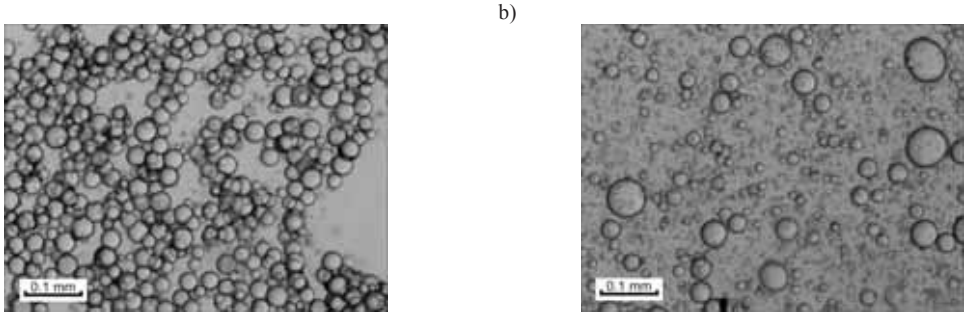


Fig. 4. Pictures of emulsions prepared with 20% oil phase (a) Na-CMC, $C_p = 2.17\%$, $M_w = 2.5 \cdot 10^5$; (b) PEO, $C_p = 0.5\%$, $M_w = 2 \cdot 10^6$

As it is shown, it is clear that analysed emulsions differed in structures and in ranges of droplet diameters. The estimated droplet diameters ranged from 6 to 40 microns for the emulsion with the Na-

CMC (Fig. 4a) and from 11 to 120 microns for the emulsion stabilized with PEO (Fig. 4b). Moreover, the flocculation of emulsion droplets was observed in the case of emulsions stabilized with Na-CMC. The estimated aggregate equivalent diameter ranged from 50 to 65 microns. The resulting channels between clusters of droplets had irregular shape and resemble converging-diverging channels. Therefore, the emulsion with this kind of structure could be used to study the effect of an extensional viscosity on the creaming process. Emulsions stabilized with PEO had a more loose structure and more variation of droplets diameters (Fig. 4b).

### *5.3. Analysis of creaming process*

In Figure 5 results of the creaming tests are presented for emulsions with the addition of Na-CMC and PEO at concentration of dispersed phase equal to 40%. The presented data in Fig. 5a show that the creaming process proceeded faster for emulsions stabilized by Na-CMC with an average molecular weight of $M_w = 2.5 \cdot 10^5$. In general, creaming is a very slow process in which small values of the shear rate occurred. As previously mentioned, the shear viscosity and extensional viscosity of aqueous solutions of polymer with molecular weights of 250,000 and 700,000 at low strain rates were comparable. Nevertheless, the creaming was faster for emulsion with polymer of molecular weight equal to $M_w = 2.5 \cdot 10^5$. It is due to that the creaming of emulsion could not be explained only by the rheological properties of the continuous phase.

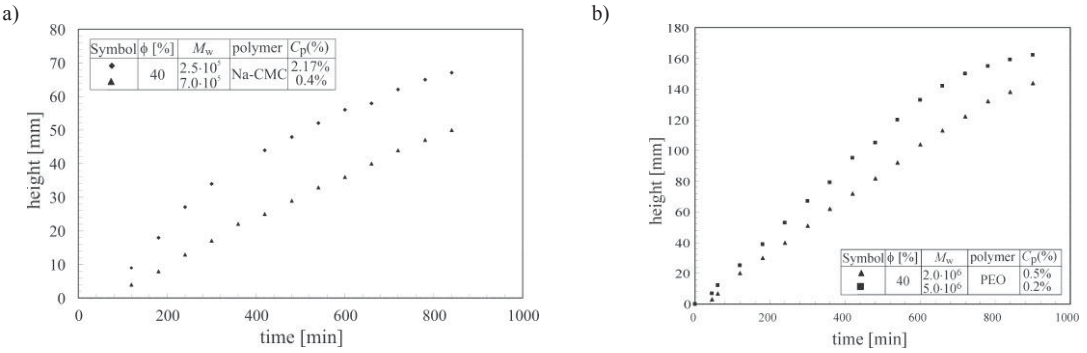


Fig. 5. Results of creaming tests in terms of height of water phase for emulsions $\phi = 40\%$ (a) Na-CMC (b) PEO

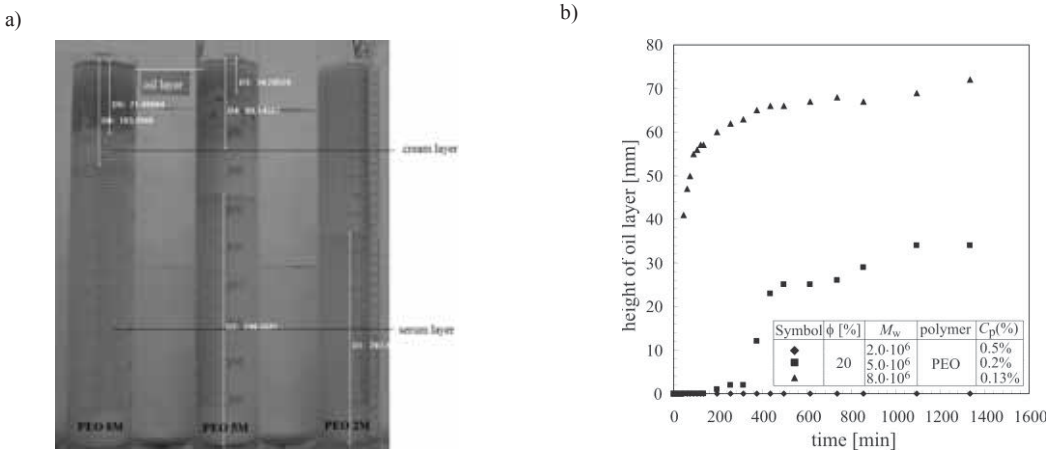


Fig. 6. Comparison of stability (creaming) test for emulsions $\phi = 20\%$ stabilized by PEO with three different average molecular weight (a) stabilization test (b) dependency of oil's height formation over a time

During the creaming tests for emulsions stabilized with PEOs with different molecular weights the clear distinction between individual phases (serum, cream and oil) was observed. The visualization of phase separation is shown in Figure 6a, while Figure 6b shows the formation of oil phase over the time. It is clear that for the emulsion stabilized by PEO with molecular weight $M_w = 8 \cdot 10^6$ the oil layer was formed rapidly and reached a constant height after approximately 600 s. In the case of emulsions with the addition of PEO with a molecular weight $M_w = 5 \cdot 10^6$ the oil layer separated also after a period of about 600s, except that the height was less than for the PEO 8M. Separation of cream layer from oil was not observed for the emulsion with PEO of smallest molecular weight. Over the timeline of creaming test the separation between the aqueous phase and cream layer was observed. Additionally, the creaming was slowest for that emulsion while the fastest was observed for emulsion with PEO $M_w = 8 \cdot 10^6$.

As previously mentioned, the concentration of PEOs were chosen in such a way that solutions of polymers in water had similar shear viscosity but differed substantially in extensional viscosity. From the data presented in Fig. 5b it is clear that creaming occurred more rapidly in solution with higher extensional viscosity (Fig. 3). Therefore, rather, it is necessary to exclude its influence on the rate of creaming. On the other hand, the data presented in Fig. 3 also show that the shear viscosity of emulsions stabilized by PEO of average molecular weight of $2 \cdot 10^6$ had the highest viscosity. These data indicate that the viscosity of aqueous solutions of PEO cannot be equated with the viscosity of the continuous phase of emulsions. In order to obtain similar values of viscosity for PEO solutions with different average molecular weights it was necessary to apply different concentrations of the polymer. Some part of the polymer is subject to adsorption on the surface of droplets of the oil phase [21]. Thus, the polymer concentration decreases in the aqueous phase which is associated with a decrease in its viscosity. In this way the reasoning is given of why creaming process occurred faster in the polymer solution with a higher average molecular weight.

## 6. Conclusions

The paper presents results of rheological measurements and analysis of creaming process of emulsions stabilized by poly(ethylene oxide). No direct relationship was observed between the extensional viscosity of the emulsions' continuous phase and rate of creaming. The results are not unequivocal. This is mainly due to the fact that it was failed to obtain an emulsion stabilized by the addition of PEO with different average molecular weights and similar shear viscosity of continuous phase. Therefore more detailed studies are planned for future.

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## References

[1] Robins MM, Hibberd DJ. Emulsion flocculation and creaming. In: Binks BP, editor. *Modern aspects of emulsion science*; London: The Royal Society of Chemistry; 1998, p 115-144

[2] Zatz JL, Ip BK. Stabilization of oil-in-water emulsions by gums. *J Soc Cosmet Chem* 1986;**37**:329-350.

[3] Yilmazer G, Kokini JL, Effect of Polysorbate-60 on the stability of O:W emulsions stabilized by propylene glycol alginate and xanthan gum. *J Texture Stud* 1991;**22**:289-301.

[4] Dickinson E. Interfacial interactions and stability of oil-in-water emulsions. *Pure Appl Chem* 1992;**64**:1721-1724.

[5] Fang Y, Dalgleish DG. Dimensions of the adsorbed layers in oil-in-water emulsions stabilized by caseins. *J Colloid Interface Sci* 1993;**156**:329-334.

[6] Dickinson E, Golding M. Rheology of sodium caseinate stabilized oil-in-water emulsions. *J Colloid Interface Sci* 1997;**191**:166-176.

[7] Pons R, Solans C, Tadros TT. Rheological behavior of highly concentrated oil-in-water (o/w) emulsions. *Langmuir* 1995;**11**:1966-1971.

[8] Pons R, Rossi R, Tadros TT. Investigation of the interaction between emulsions and suspensions (suspoemulsions) using viscoelastic measurements. *J Phys Chem* 1995;**99***:*12624-12630.

[9] Cheng JT. Particle structure of PVC based on cellulosic suspension system. *J Macromol Sci Phys* 1981;**B20***:*365-380.

[10] Hayakawa K, Kawaguchi M, Kato T. Protective colloidal effects of hydroxypropyl methyl cellulose on the stability of silicone oil emulsions. *Langmuir* 1997;**13**:6069-6073.

[11] Meller A, Stavans J. Stability of emulsions with nonadsorbing polymers, *Langmuir* 1996;**12**:301-304.

[12] Dontula P, Pasquali M, Scriven LE, Macosko ChW. Can extensional viscosity be measured with opposed-nozzle devices?. *Rheol Acta* 1997;**36**:429-448.

[13] Gauri V, Koelling KW. Extensional rheology of concentrated ply(ethylene oxide) solutions. *Rheol Acta* 1997;**36**:555-567.

[14] Pal R. Rheology of polymer-thickened emulsions. *J Rheol* 1992;**36**(7):1245-1259.

[15] Pal R. Rheological properties of emulsions of oil in aqueous non-Newtonian polymeric media. *Chem Eng Comm* 1992;**111**:45-60.

[16] Diftis N, Kiosseoglou V. Improvement of emulsifying properties of soybean protein isolate by conjugation with carboxymethyl cellulose. *Food Chemistry* 2003;**81**:1-6.

[17] Metzner AB, Park MG, Turbulent flow characteristics of viscoelastic fluids. *J Fluid Mech* 1964;**20**:291-303.

[18] Virk PS. Drag reduction fundamentals. AIChE J 1975;**21**:625-656.

[19] Kiss D, Karoly S, Marek T. Tracking the physical aging of poly(ethylene oxide): A technical note. *AAPS Pharm Sci Tech* 2006;**7**(4):Article 95

[20] Różańska S. Extensional viscosity of w/o emulsions, 20th International Congress of Chemical and Process Engineering CHISA 2012, No. 371.

[21] Dickinson E. Hydrocolloids as emulsifiers and emulsion stabilizers. *Food Hydrocoll* 2009;**23**:1473-1482.